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THE ROLE OF THE MODIFYING CHROMIUM ION IN THE STRUCTURE OF MAGNESIAN SPINEL (A Review)

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The factors determining the principles of filling the polyhedrons in spinels with cation components are considered. An attempt is made to explain the variation in the color range of magnesian spinel modified with chromium ions. A hypothesis for two coordination states of chromium (four and six coordination) in the structure of magnesian spinel is put forward and justified.

The development of the theory establishing the principles of filling the spinel polyhedrons with cation components is of great theoretical and practical value. The effect of the modifying ion on the structure and properties of the mineral depends on the position this ion takes in the crystal unit.

The authors studied the effect of a modifying chromium ion on the structure of magnesian spinel.

The spinel unit has a face-centered cubic unit cell containing 8 units. The structure is based on extremely close cubic packing consisting of oxygen anions, and each unit cell contains 32 octahedral and 64 tetrahedral vacancies per 32 oxygen anions. Only 16 octahedral and 8 tetrahedral vacancies out of the total number of 96 vacancies are occupied by metal cations, i.e., the oxygen points are completely filled, while only one-eighth of the tetrahedral and half of the octahedral unit points are occupied. When the stoichiometry is disturbed, these relationships between filled and vacant unit points are not fulfilled. Depending on the distribution of metal cations between the octahedral and tetrahedral positions, normal, inverse, and mixed spinels are distinguished [1].

In normal spinels, the two-charge metal cations X^{2+} are positioned in the tetrahedral vacancies, and the three-charge cations Y^{3+} are located in the octahedral vacancies. The overall structural formula of these spinels can be written in the form of $X_{[4]}^{2+} Y_{[6]}^{3+} O_4$ (the bottom index means the oxygen coordination number of the cation).

In the inverse spinels, cations X^{2+} and part of cations Y^{3+} occur in the octahedral vacancies, and the rest of Y^{3+} cations occur in the tetrahedral vacancies, which agrees with the formula $X_{[6]}^{2+} Y_{[4]}^{3+} Y_{[6]}^{3+} O_4$.

The mixed spinels are described by the formula $\left(X_{1-z}^{2+} Y_z^{3+} \right) \left(X_z^{2+} Y_{2-z}^{3+} \right) O_4$. In these spinels, the cations of bivalent and trivalent metals can simultaneously occur in the tetrahedral and octahedral positions, and parameter z determining the share of the cations Y^{3+} filling the tetrahedral positions acts as the extent (degree) of inversion of the spinel structure (at $z = 0$, the spinel is normal, and at $z = 1$, the spinel is inverse) [2].

Two types of disturbance in stoichiometry are found in the spinel: σ and γ -nonstoichiometry (according to Presedskii): σ -nonstoichiometry reflects a deficiency or excess of oxygen; and γ -nonstoichiometry points to an imbalance in the ratio between the cation components of the crystal, which is manifested when oxide is removed from the crystal (or incorporated in the crystal). Specific defects arise in the case of γ -nonstoichiometry evolving at high temperatures [3].

Natural spinels are usually normal, and artificially synthesized spinels are inverse or partially inverse (i.e., mixed, since in long-term annealing, partial stabilization takes place) due to the fact that synthesis proceeds at high temperatures, and γ -nonstoichiometry is caused by removal of X^{2+} from the crystal [2]. At temperatures above 1000°C, a considerable excess of Al_2O_3 is observed in aluminomagnesian

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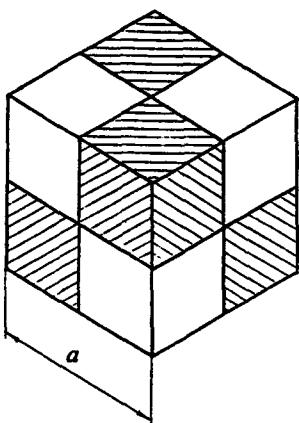


Fig. 1. Arrangement of cations in octants.

spinel, as a consequence of which the ratio between the oxides no longer satisfies the law of equivalents.

A system in which one of the oxides is in excess and the other is insufficient, while the spinel phase retains its structure and remains homogeneous, can be regarded as a solid solution, in which the spinel is a solvent and the excessive oxide is the dissolved agent.

Each anion in the spinel is surrounded by one X and three Y cations. Each X cation is surrounded by anions spaced at a distance of $1/8$ of the space diagonal of the unit cell, i.e., $\frac{1}{8}a\sqrt{3}$, (a is the unit cell parameter). The coordination polyhedron for the X-cations is a tetrahedron. Each Y-cation is surrounded by 6 anions spaced at a distance of $a/4$, and its coordination polyhedron is an octahedron. Thus, the structure of the spinel is constructed of tetrahedrons and octahedrons, and each oxygen ion belongs to one tetrahedron and three octahedrons.

If the unit cell of the spinel is by convention split into 8 octants, the anions will be placed equally in all octants: each octant will have 4 anions forming a tetrahedron. Contrary to this, the arrangement of the cations coincides only in the non-adjacent octants having one common edge, i.e., only in the shaded, or only in the non-shaded octants (Fig. 1) [4].

The tetrahedral A-points form geocentric cubic units (GCC) with the edge a , which are shifted with respect to each other by $\frac{a}{4}\sqrt{3}$ towards the space diagonal of the cube,

i.e., an alias structure. The X-cations in the right octant are located in the center and in 4 out of 8 vertexes, and in the left octant they occupy the other four vertexes, while the central vacancy is not occupied by an ion.

The octahedral B-points are arranged in the points of the four interpenetrating GCC lattices with edge a , which are shifted with respect to each other by a distance of $\frac{a}{4}\sqrt{2}$ toward the cube diagonals. The B-points are arranged only in the non-adjacent octants. Together with the oxygen ion, they

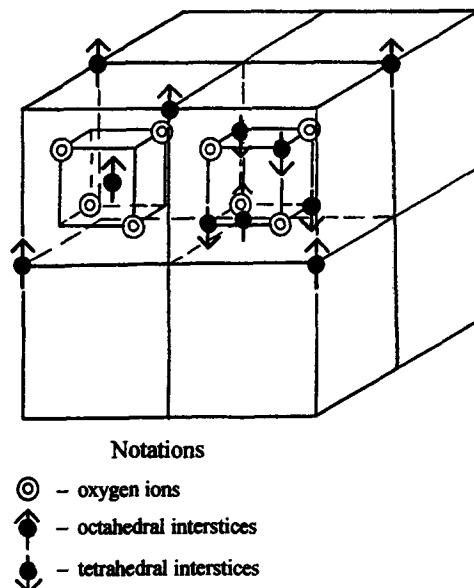


Fig. 2. A- and B-sublattices in the spinel structure.

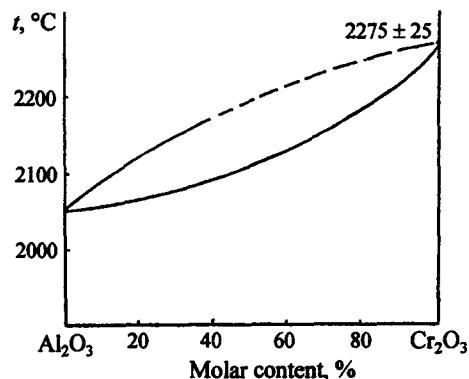


Fig. 2. Phase diagram of the $\text{Al}_2\text{O}_3 - \text{Cr}_2\text{O}_3$ binary system.

form a cube with the edge $a/4$ in the occupied quadrant (Fig. 2).

Thus, there are two different cation subunits in the spinel structure: the tetrahedral A-lattice and the octahedral B-lattice.

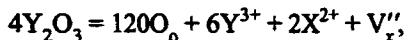
A single unit cell contains four "floors" of tetrahedral vacancies arranged over each other. The chain arrangement of the vacancies is observed in all directions. The structure contains two types of cation layers: layers consisting purely of X cations, and mixed layers consisting of X and Y cations.

The bonds in the spinel structure are mixed, i.e., ionic and covalent.

The nature of defect formation significantly depends on which of the oxides dissolves better in the spinel and in what way dissolution of the excessive oxide proceeds. Most often, the solubility of a compound of the Y_2O_3 and $\text{X}^{2+}\text{Y}^{3+}\text{O}_4$ type is many times greater than the solubility of oxides of the

XO type. Magnesium oxide virtually does not dissolve in aluminomangesian spinel modified with chromium oxide, while the solubility of aluminum and chromium oxides at high temperatures can be significant. This is probably due to the fact that MgO has a significantly higher melting point (2800°C) than aluminum and chromium oxides (2050 and 2300°C, respectively). According to the data in [5], Cr₂O₃ and Al₂O₃ form a series of continuous solutions (Fig. 3). Each of the oxides in the spinel tends to behave in an individual manner. This is manifested by the fact that in heat treatment, it is magnesium oxide that evaporates first, since its evaporation capacity is significantly higher than that of the more heat-resistant aluminum and chromium oxides [4, 6, 7].

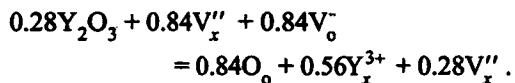
The completion of a spinel unit of the XY₂O₄ type by enriching it with oxides of the Y₂O₃ type has to be implemented in keeping with the principle of the equivalence of different types of unit points. Filling of four oxygen points causes the appearance of two equivalent Y³⁺ points and one X²⁺ point in the unit. There are three cation points for every 4 anion points. Therefore, the introduction of 4 molecules of a compound of the Y₂O₃ type will cause filling of 12 oxygen points, six Y³⁺ points, and only two X²⁺ points, instead of the equivalent three X²⁺ points. One X²⁺ point will inevitably be left vacant



i.e., no oxygen vacancies arise.

According to the data of R. Collong [8], aluminomagnesian spinel at 1900°C has a limit composition of 0.16MgO · 1.28Al₂O₃. As a result, magnesium oxide is deficient and aluminum oxide is in excess with respect to the stoichiometric composition.

The red or pink color of the spinel is related to isomorphous substitution of Cr³⁺ ions for Al³⁺ ions in the structure of the spinel (absorption bands at 25,600 and 18,700 cm⁻¹) [4]. Had the excess Y³⁺ completed its subunit, i.e. had it been positioned in the octahedral points, then in a state of equilibrium 84% of the tetrahedral points would have been vacant, which is unlikely, since the other cation subunit is overpopulated. The tetrahedral vacancies are filled with excess Y³⁺ according to the following scheme: two-thirds of the vacancies disappear and only one-third remains vacant [9]:



In the context of thermodynamics, this process can be considered as a solid solution of the cations Y³⁺ introduced in the oxygen structure of the crystal, since the rigid cubic unit of oxygen containing octahedral and tetrahedral vacancies has a decisive role in the formation of the spinel structure [10, 11].

At high temperatures of synthesis, the ability of the oxygen unit to retain metal ions in the unit points becomes weaker, since with a temperature increase, the probability of the metal ions leaving their places increases, especially for the tetrahedrons, since most cations are more strongly bonded in the octahedrons that in the tetrahedrons.

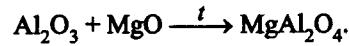
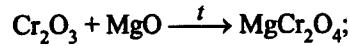
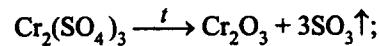
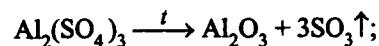
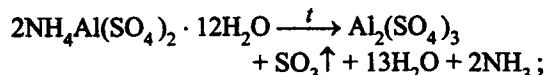
Thus, in synthesis of minerals, vacancies arise in the tetrahedrons of the crystal, and Y³⁺ ions accumulate in excess with respect to stoichiometry. According to Blasse [3, 9], it is more convenient to have either large ions with a low charge, or small ions with a high charge in the tetrahedral positions, since with an increase in the charge level, the ion radii decrease and migration of cations with 3+ oxidation to the tetrahedral position is reasonable.

In aluminomagnesian spinel, both cations (magnesium and aluminum and, consequently, chromium which isomorphically replaces aluminum) in normal conditions, according to the Reznitskii series, occupy the tetrahedral and octahedral positions, respectively (in conformity with the energy of preference for the octahedron and tetrahedron). In synthesis, this equilibrium is disturbed, and cations Y³⁺ migrate from the octahedrons to the tetrahedrons [12, 13].

In order to verify the above reasoning, magnesian spinel modified with chromium oxide was synthesized. For this purpose, the following compositions were prepared: 1 — reference composition (without introduction of the modifying ion); 2 — 0.5 wt.% Cr₂O₃ (above 100%); 3 — 1.0 wt.% Cr₂O₃ (above 100%).

The initial materials were ammonium alum, magnesium and chromium sulfates. Synthesis was carried out employing low-temperature plasma as a high-temperature source. The parameters of a UPU-3 plasma gun with a GN-5p burner in synthesis of the minerals were as follows: voltage of 30–32 V, current strength of 300–500 A. The flow rate of the water used for cooling of the plasma gun was 10–12 liter/min. Argon at a pressure of 0.27–0.29 MPa served as the plasma-forming gas. The consumption of argon was 25–27 liter/min.

The following reactions occurred in synthesis:



According to the data in [14], the similarity in the structures and the unit parameters of many spinels is responsible for their peculiar feature, namely, the facility of formation of solid solutions of replacement (spinelides) between them.

For example, unlimited solubility was established for crystals of $MgAl_2O_4$ and $MgCr_2O_4$, for $FeCr_2O_4$ and $FeFe_2O_4$, etc. Complete isomorphous mixability in spinels is observed for Mg^{2+} and Fe^{2+} , and aluminum can be replaced with Fe^{3+} and Cr^{3+} with formation of solid solutions between aluminum and chromium spinels.

The crystalline phases and the structure of the samples obtained were investigated by x-ray phase analysis (DRON-3 diffractometer, rate of exposure of 2° per 1 min, exposure mode from 5 to 64°).

The x-ray phase analysis indicated that the minerals obtained belong to the class of spinels, as was indicated by the respective peaks. The following crystalline phases were identified: $MgAl_2O_4$ and $\alpha-Al_2O_3$, which were clearly expressed in all samples. This is supported by the data from [15] describing the formation of solid solutions of spinel with oxides of trivalent metals, i.e., $MgAl_2O_4$ with the α -form of Al_2O_3 , whose crystal unit is similar to the spinel unit.

In order to determine the parameters of the unit of spinel and reveal the effect of the chromium ions as they are incorporated in the spinel structure, the diffraction patterns of the analyzed samples were made, with exposure angles from 99 to 101° . This supplied the necessary data for calculation of the unit cell parameters for the synthesized samples.

The calculations were performed according to the formula [16, 17]:

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{A^2},$$

where d is the interplanar distance, E; h , k , and l are the crystallographic indexes of the faces (Miller indexes); A is the size of the unit cell, E.

The calculation results are given in Table 1.

According to [13], the changes in the cell parameters in isomorphic substitutions depend linearly on the change in the isomorphic impurity content, obeying Vegard's law. It is seen from Table 1 that as the content of the modifying chromium ion increases, the cell parameters increase as well. It can be inferred that Al^{3+} with an ionic radius of 0.057 nm is isomorphically replaced by Cr^{3+} with an ionic radius of 0.064 nm. In this case, complete isomorphism takes place, since according to [14], when the difference in the ionic radii is below 10%, a series of continuous solid solutions is formed.

The increase in the unit cell parameters is determined by the fact that the ionic radius of chromium is bigger than that of aluminum. The chromium ion replaces the aluminum ion not only in octahedrons, but in tetrahedrons as well. This is probably related to the variations in color in spinels with different chromium contents. According to the data of Bender

TABLE 1

Parameter	Composition		
	1	2	3
Interplanar distance, E	1.01570	1.01696	1.01771
Unit cell parameter a , E	8.14203	8.15276	8.15817
Distance, E:			
between X-cations and anions	1.7628011	1.7651242	1.7662955
between Y-cations and anions	2.0355075	2.03819	2.0395425
Displacement of A-nodes parallel to spatial diagonal of the cube, E	3.5256022	3.5302485	3.532591
Displacement of B-nodes parallel to spatial diagonal of the cube, E	2.878642	2.8824357	2.8843485

and Zeeman, when the molar content of Cr_2O_3 is up to 8%, it enters the lattice of ruby and imparts a red color. With an increase in the chromium content, the color changes to green. A similar phenomenon is observed in spinels.

Doping of spinels with chromium alters their color depending on the ratio of $MgO : Al_2O_3$: with the ratio of 1 : 1, the color is red; with the ratio of 1 : 2, it is greenish-brown; with 1 : 3, it is brown, and with 1 : 6, it is dark green [15, 16]. It can be inferred that the chromium ions primarily tend to occupy positions in tetrahedral vacancies (filling of octahedral positions proceeds simultaneously but with lower intensity), which determines the red color.

With an increase in the chromium content, the tetrahedral positions get saturated and filled, and the chromium ions, having filled the tetrahedrons, begin filling the octahedrons with higher intensity, and considering that the number of octahedral positions is higher than that of tetrahedrons, their gradual filling results in their predominance, and the color is gradually transformed into green. The change in color depending on the ratio of $MgO : Al_2O_3$ can be indirect evidence of this assumption; the higher the content of MgO in the composition, the more tetrahedral vacancies emerge, and, accordingly, chromium ions dominate, and consequently, the color is red. On the other hand, a decrease in the content of MgO causes prevalence of "octahedral" chromium ions and the color is green, i.e., the chromium ions in the structure of the spinel exist in two coordination states (6 and 4), and the predominance of one over the other determines the spinel color.

The priority of filling the tetrahedral positions for chromium ions is also due to the fact that it is more advantageous to have low-charge large ions in the tetrahedral positions, and as the ionic radius of chromium is larger than the aluminum ionic radius, chromium ions are preferred in filling of tetrahedral positions. Moreover, chromium cations can occupy tetrahedral positions with greater facility because they are larger than the octahedral vacancies, since the ionic radius of magnesium is larger than the ionic radius of aluminum, and incorporation of chromium ions requires lower consumption of energy.

To summarize, it can be stated that two methods exist for producing spinels of different colors:

an increase (decrease) in the content of chromium oxide in the initial mixture;

variation of the time of high-temperature treatment and the treatment temperature.

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